(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 518 073 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent: **11.11.1998 Bulletin 1998/46**

(51) Int Cl.6: **C08F 214/22**, C08F 214/26

(21) Application number: **92108209.5**

(22) Date of filing: **15.05.1992**

(54) Fluoroelastomers based on vinylidene fluoride exhibiting superior resistance to organic bases

Fluoroelastomere auf Basis von Vinylidfluorid mit einer überlegenen Beständigkeit gegen organische Basen

Elastomères fluorés à base de fluorure de vinylidène montrant une résistance supérieure aux bases organiques

(84) Designated Contracting States:
AT DE DK ES FR GB GR IT NL SE

(30) Priority: **15.05.1991 IT MI911339**

(43) Date of publication of application:
16.12.1992 Bulletin 1992/51

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(56) References cited:
EP-A- 131 308
EP-A- 335 705
DE-A- 2 132 463
FR-A- 2 305 462
US-A- 3 449 305
US-A- 4 694 045

- **CHEMICAL ABSTRACTS, vol. 88, Columbus, Ohio, US; abstract no. 122446N, &JP-A-52134696 [ASAHI GLASS KK]**

Remarks:
The file contains technical information submitted after the application was filed and not included in this specification

EP 0 518 073 B1

Description

The present invention relates to novel fluoroelastomeric copolymers based on vinylidene fluoride (VDF), and comprising ethylene and tetrafluoroethylene units, exhibiting high mechanical characteristics combined with a high resistance to chemicals, especially to nucleophilic agents and polar solvents.

The problem to be solved is to find a VDF based fluoroelastomer having the combination of properties indicated. In fact it is well known that the most common fluoroelastomers, i.e. VDF-based fluoroelastomers, comprising VDF/HFP copolymers and VDF/HFP/TFE, are not resistant to nucleophilic agents in a satisfactory way.

European Patent Application 335,705 describes elastomeric compositions vulcanizable with particular systems based on polyhydroxylated compounds and organoonium compounds, wherein the elastomeric polymer consists of units of vinylidene fluoride (VDF), tetrafluoroethylene (TFE) and an olefin, preferably propylene, whereas hexafluoropropene (HFP) units must be absent.

Said patent application states that the presence of hexafluoropropene units in VDF fluoroelastomers brings to fluoroelastomers which are attacked by nucleophilic agents. The deleterious effect induced under this respect by HFP, in VDF based fluoroelastomers, is also confirmed by Dennis E. Hull in "Elastomerics", January 1990, pages 11-16, and by W.M. Grootaert, Werner M., Kolb, Robert E. and Worm, Allen T., 1989, presented at the 1989 ACS Rubber Division Conference.

According to the last mentioned work, compositions of the type described in European Patent Application 335,705 are resistant to amine containing motor oils.

In the products described in such patent application, however, good elastomeric properties can be only obtained with a high hydrogenated olefin monomer content. This is at the expense of product stability toward swelling in oil.

Fluoroelastomeric polymers consisting of units derived from ethylene (E), TFE and perfluoroalkylvinylether (PAVE) are described in US Patent 4,694,045. These fluoroelastomers are said to possess high resistance to amines and strong bases, in addition to a good balance of properties at high and low temperatures.

These products exhibit however the disadvantage of not possessing the good processability characteristics deriving from the presence of VDF units. For this same reason, they are not suitable for ionic vulcanization with conventional crosslinking systems, and finally they require high alkylvinylether contents, at the expense of the product economics.

European Patent Application 131,308 describes terpolymers derived from tetrafluoroethylene, perfluoroalkylvinylethers and vinylidene fluoride, the last being in an amount not greater than 2% in moles based on the total moles. Vinylidene fluoride functions as a site for ionic vulcanization performed with non-conventional vulcanizing systems based, for instance, on polyhydroxylated compounds, in particular Bisphenol AF, and specific accelerators of the type of cyclic polyethers. According to this patent application, in order to obtain terpolymers exhibiting satisfactory resistance to amines, the vinylidene fluoride content should not exceed 0.4% in moles.

In US Patent 4,368,308 fluoroelastomeric polymers are described having resistance to chemicals, and to oils, as well as low-temperature resistance. Said polymers contain units of fluorovinylether ((FV) and ethylene (E), in a molar ratio E/FV comprised between 95/5 and 30/70, with a total FV + E contant of at least 70% in moles, wherein the possible balance to 100 may consist of other monomeric units deriving from TFE, VDF, HFP, chlorotrifluoroethylene etc.

Due to the predominant ethylene and perfluorovinylether content, the polymers of US Patent 4,368,308 cannot be obtained with molecular weights sufficiently high to render them useful for practical applications.

Further, Chemical Abstracts, vol. 88, Abstract no. 122 446 n discloses fluorine containing elastomers, which contain as structural units in moles: 30-70% of vinylidene fluoride, 3-30% of propylene, 15-45% of ethylene tetrafluoride and 2-20% of fluorovinyl ether.

The object of the present invention is to provide novel elastomeric copolymers based on vinylidene fluoride, exhibiting high resistance to bases and alcohols, and in particular to amine containing oils, combined with optimal and elastomeric properties and having good processability. These copolymers comprise, in addition to VDF monomeric units, also monomeric units deriving from TFE, from ethylene (E) as well as from hexafluoropropene (HFP). Said monomeric units are present in the following molar percentages:

VDF	4-75%
HFP	12-40%
(E)	2-35%
TFE	2-60%

Copolymers wherein the HFP units are partly substituted by perfluoromethylvinylether (MVE) units are preferred.

As already mentioned above, copolymers of this invention, in addition to high elastomeric characteristics and processing properties deriving from the presence of VDF units, show superior resistance to nucleophilic agents, for example especially to amines and amine containing oils, and also to polar solvents, for example alcohols.

The spectra of the elastomeric copolymers according to the invention, from NMR ^{19}F analysis carried out in hexadeuteroaceton at room temperature with a spectrometer at 288 MHz, present peaks corresponding to "Chemical Shifts" of 96.3 ppm and 74.6 ppm, which can be respectively associated with the following structures:

$$CH_2CF_2CH_2CH_2;\ CF_2CF(CF_3)CH_2CH_2.$$

These structures respectively correspond to the following monomeric diads:

a) $-CH_2-CF_2-CH_2CH_2-$ (VDF)-(E)

b) $-CF_2-CF(CF_3)-CH_2CH_2-$ (HFP) - (E)

The above mentioned diads appear, in the copolymers according to this invention, together with other typical diads for copolymers based on VDF, of the Prior Art, such as:

d) $-CF_2-CF(CF_3)-CH_2-CF_2-$ (HFP) - (VDF)

e) $-CF_2-CF_2-CH_2-CF_2-$ (TFE)-(VDF)

The structures:
$CF_2CF(CF_3)CH_2CF_2$; $CH_2CF_2CF_2CF_2CH_2$; which can be associated, respectively, to "Chemical Shifts" of 75.3-75.5 ppm and 124-126 ppm, correspond to such sequences.

In the copolymers of the present invention there are also present (E)-(TFE) sequences, which can be identified by I.R..

The method of analysis consists in this case in preparing a copolymer film on a potassium bromide disk by evaporation from a copolymer solution in acetone and then examining the film in a FT-IR spectrometer.

By this technique it is possible to identify (E)-(TFE) sequences on the basis of the absorbances at 2880 cm^{-1} and at about 1450 cm^{-1} (1545 cm^{-1}) due to bending of CH_2 groups.

What said below concerning the NMR ^{19}F peak identification in the presence of additional monomeric units, different from those of the present invention, also applies to the identification of the IR bands for E-TFE.

The above mentioned peaks can vary in intensity depending on the concentration of the corresponding monomeric sequences and can be determined without difficulty at very low concentrations of such sequences.

In particular the above indicated peaks can be easily determined in the copolymers according to the invention obtained by polymerization in the presence of dispersions, emulsions or microemulsions of perfluoropolyoxyalkylenes in water utilizing the above mentioned comonomers. In particular, for the copolymer in example 1, obtained at the therein indicated temperature and pressure conditions, the frequencies at which the above indicated peaks appear can be easily determtined.

The introduction of comonomers different from those mentioned above, which do not alter the above indicated resistance properties to organic bases and polar solvents, e.g. alcohols, nor the mechanical properties ac low temperatures, could, however, alter or even determine the disappearance of the peak, for example for overlapping.

Obviously also the thus modified polymers come within the spirit and scope of the present patent application.

According to the present invention the term typical "peak" for the above indicated monomeric diads by NMR ^{19}F analysis, also comprises the band determined by such peak.

For fluoroelastomeric copolymers according to the present invention, it is meant elastomers having preferably amorphous structure. However it can be also present a few percentage of crystallinity, in general up to 1-2% by weight. For elastoplastic applications however it can also be present a higher percentage of crystallinity, for example 8-10% or even 30-50% by weight; in this case very good mechanical properties can be obtained.

The copolymers of the present invention are those obtained with ethylene, vinylidene fluoride, hexafluoropropene,

and tetrafluoroethylene, possibly also comprising MVE, and possibly modified with different additional monomers, as mentioned herein.

According to another embodiment of the present invention, the HFP units in the copolymer can be wholly substituted by perfluoromethylvinylether (MVE) units, with the proviso that, when the sum of MVE and ethylene (E) units is equal to or higher than 70 %, the copolymer has a molecular weight sufficiently high to give a Mooney viscosiy of at least 10 $ML(1+10)^{121}$, preferably of 20 to 60 $ML(1+10)^{121}$, and contains sequences consisting of monomeric diads VDF-E.

Elastomric polymers according to this invention can advantageously also comprise units deriving from iodine and/or bromine containing copolymerizable monomers, such as for instance iodo and/or bromo olefins containing from 2 to 10 carbon atoms, or fluoro-iodo and/or bromoalkylvinylethers, for example BVE, in an amount usually comprised between 0.05 and 2 moles per 100 moles of all the other monomeric units.

Furthermore the polymeric chains can contain iodine and/or bromine atoms at the end of the polymeric chain.

The preparation of the copolymers object of the present invention can be accomplished by polymerization of the monomers in emulsion in accordance to conventional techniques, preferably in the presence of radical initiators such as for example persulphates, perphosphates, perborates or alkaline or ammonium percarbonates, possibly in combination with reducing agents such as alkaline metal or ammonium sulphites, bisulphites, hyposulphites, phosphites, hypophosphites, or in combination with ferrous, cuprous or silver salts, or with other easily oxidable metal salts.

Surfactants, such as for example ammonium perfluorooctanoate, or other agents known to be suitable for the preparation of fluoroelastomers can be present in the polymerization medium.

Chain transfer agents can be used in general as molecular weight regulators. Comprised among them are chain transfer agents which contain iodine and/or bromine, such as for instance compounds having general formula $Rf(I)_x(Br)_y$ (Rf= perfluorinated hydrocarbon radical containing from 1 to 8 carbon atoms; x,y = integers comprised between 0 and 2, with at least x or y = 1 and $x+y \leq 2$). Alkaline or alkaline earth metal iodides and/or bromides can be used as well, in accordance to what described in European Patent Application 407,937.

At the end of the polymerization, the fluoroelastomer is isolated from the polymeric latex by known methods, such as by coagulation by addition of electrolytes or by cooling.

The polymerization reaction can also be carried out in bulk or in an organic liquid containing an organic free radical initiator.

The polymerization reaction is generally carried out at temperatures comprised between 25 and 150 °C, under pressures up to 10 MPa.

The preparation of elastomeric copolymers according to the invention is preferably carried out by polymerization in the presence of a microemulsion formed by one or more perfluoropolyoxyalkylenes and water, in accordance to the method described in European Patent Application 250,767.

The polymerization can be advantageously carried out also employing, Instead of a microemulsion, an emulsion or dispersion of perfluoropolyoxyalkylenes and water in accordance to the method described in US Patent 4,789,717.

Other emulsions and dispersions of perfluorooxyalkylenes and water are described for instance in European Patent Applications 196,904, 280,312 and 360,292.

The copolymers of the present invention can be advantageously vulcanized using peroxidic methods when such copolymers contain iodine and/or bromine atoms on the chain and/or at a terminal position in the macromolecule. Peroxidic systems which can be used are well known in the Art, see for example European Patent Application 136,596.

The vulcanization of the copolymers of the invention can also be accomplished, preferably, using ionic methods.

The vulcanizing and accelerating agents are well known in the Art, for example, those described in US Patent 3,876,654, US Patent 4,259,463 and in European Patent Application 335,705.

Vulcanizing agents which can be cited in particular are aromatic or aliphatic polyhydroxy compounds and derivatives thereof.

They can be di-, tri- and tetrahydroxy-benzenes, naphthalenes, antracenes. Bisphenols in which the two aromatic rings are linked through a bivalent aliphatic, cycloaliphatic, aromatic radical having from 1 to 13 carbon atoms can also be used; or the linking radical is oxygen, sulphur, carbonyl, etc.. The aforementioned aromatic ring or rings can also be substituted with one or more chlorine, or fluorine, or bromine atoms, or by carbonyl, alkyl, acyl groups. See in particular European Patent Application 335,705 and US Patent 4,233,427.

As accelerators the ones cited in European Patent Application 335,705 can be employed, for example those indicated in US Patent 3,876,654 and US Patent 4,259,463.

However all accelerators indicated in European Patent Application 335,705 can be used.

The following can be indicated:

$$\left[\begin{array}{c} R^3 \\ | \\ R^2 - Q - R^4 \\ | \\ R^5 \end{array}\right]_n X^{-n}$$

wherein

Q is N, P, As, Sb,
X is the organic or inorganic anion indicated in the cited European Patent Application, for instance chloride sulphate, acetate, phosphate, phosphonate, hydroxide, alkoxide, phenoxide, bisphenoxide; n is the anion valence; R^2, R^3, R^4, R^5 are alkyl, aryl groups or a combination thereof.

Various representative examples are indicated in the cited European Patent Application.
The class of amino-phosphonium salts is described in US Patent 4,259,463.
Other accelerators are the phosphoranes known in the Art, for instance in US Patent 3,752,787.
Additional accelerators are indicated in European Patent Application 182,299 A2 and 120,462 A1. Accordingly, the present invention is directed also to an elastomeric copolymer obtained from a copolymer of said invention by ionic vulcanization, which is carried out with Bisphenol. AF and a quaternary phosphonium or ammonium salt.

Mixed vulcanizing systems can be used as well, for instance ionic and peroxidic vulcanizing systems, as indicated in European Patent Application 136,596.

The following examples serve to illustrate the object of the present invention without having a limitative value. In the examples the following compounds are used:

- Luperco 101 XL, sold as Lupercox[R] by Pennwalt,
- Taic: triallylisocyanurate
- TB PCL: tetrabutylphosphonium chloride.

<u>Preparation of a Microemulsion formed by a Perfluoro-polyoxyalkylene and Water.</u>

14.5 ml of the compound having formula:

$$CF_3O(CF_2-\underset{\displaystyle CF_3}{\underset{|}{CF}}O)_n(CF_2O)_mCF_2COOH$$

obtained according to European Patent Application EP 340,740 (Galden acid by Ausimont S.p.A.) having an average molecular weight = 600, are mixed with 14,5 ml of 30% by volume NH_4OH in a glass container equipped with a stirrer operating under moderate stirring conditions. 29 ml of demineralized H_2O are subsequently added.
8.9 ml of the product having formula:

$$CF_3O(CF_2-\underset{\displaystyle CF_3}{\underset{|}{CF}}O)_n(CF_2O)_mCF_3$$

and having an average molecular weight of 450 are added to the thereby obtained solution.
A thermodynamically stable clear solution, microemulsion, is obtained by heating to a temperature of 85 °C.

<u>Example 1</u>

To a 10 l reactor in vacuum condition, equipped with a stirrer operating at 545 rpm, 6,500 g of water are added and the reactor is brought to pressure by a monomeric mixture having the following molar composition:

VDF	18%
HFP	29%
MVE (perfluoromethylvinylether)	34%
E (ethylene)	5%
TFE	14%

The operating temperature is 85 °C and the pressure is 22 relative bar.
Thereafter the totality of the previously described microemulsion, heated to 85 °C, is added and thereafter, in sequence:

- 13 g of ammonium persulphate (PSA), dissolved in water, 6.5 g of which added at the beginning and the remainder subdivided into 9 portions, of 0.72 g each, each added at every 10% conversion;
- 46 g of 2-bromoperfluoroethylvinylether, subdivided into 20 additions, of 2.3 g each, the first one executed before initiating the polymerization, and the subsequent ones at every 5% conversion;
- 6.4 g of CH_2I_2 (chain transfer agent) subdivided into 4 additions, of 1.6 g each, the first one executed at the beginning of the polymerization and the others at every 25% of monomer conversion.

A constant pressure is maintained during the polymerization, feeding the monomers in the following molar ratios:

VDF	23.5%
HFP	6.5%
MVE	16.0%
E	28 %
TFE	26 %

2,900 g of polymer are obtained after 204 minutes. The reactor is cooled to room temperature, the emulsion is discharged and coagulated by addition of an aqueous solution of aluminum sulphate.
The polymer is separated, washed in water and dried in an air circulating oven at 60 °C for 24 hours.
Table 1 reports data concerning the qualitative and quantitative composition of the polymer, the T_g and Mooney viscosity values, as well as the presence of some sequences of monomeric diads as determined by NMR ^{19}F and IR.
Table 2 reports data concerning the formulation utilized for vulcanizing the polymer, the characteristics of such formulation, as well as those of the polymer as vulcanized, after post-vulcanization in an oven at 230 °C for 24 hours, and of its resistance to testing in amine containing oil, in the hereafter defined conditions.
Vulcanization of the polymer has been carried out in a press at 170 °C for 10 minutes.

Example 2

Operating conditions are in accordance with Example 1 with the difference that BVE is not added to the reaction mixture during the polymerization.
After a polymerization time of 157 minutes, 2,290 g of polymer are obtained.
Table 1 and 2 report the characteristics of the polymer, of the composition of the vulcanizing formulation and of the vulcanized product.

Example 3

The reactor described in Example 1 is used, is brought to pressure with a monomeric mixture having the following molar composition:

VDF	29%
HFP	41%
MVE	13%
TFE	14%
ETHYLENE	3%

The operating temperature is 85 °C and the pressure is 22 relative bar.

Feeding of the microemulsion and of PSA is carried out in accordance to Example 1.
A total of 11.9 g of ethyl acetate as chain transfer agent are further added, 5.9 g of which at 5% monomer conversion, and the remainder subdivided into 4 additions of 1.5 g each, executed at 25%, 45%, 65% and 80% conversion, respectively.
The pressure is maintained constant during the polymerization by feeding a monomer mixture of the following molar composition:

VDF	40%
HFP	14%
MVE	7%
E	20%
TFE	19%

After a 206 minutes time, 2,900 g of polymer are obtained. Tables 1 and 2 report the data concerning the characteristics of the polymer, the vulcanizing formulation and the vulcanized product.

Example 4

Operating conditions are as in Example 1 with the exception that no microemulsion is added and that the reactor pressure is attained using a mixture having the following molar composition:

VDF	43%
HFP	29%
MVE	16%
E	3%
TFE	9%.

The pressure is maintained constant during polymerization by feeding a monomer mixture having the following molar composition:

VDF	60.5%
HFP	14.5%
MVE	7%
E	8%
TFE	10%

After 90 minutes polymerization time 3,000 g of polymer are obtained.
Table 1 reports the characteristics of the obtained polymer.
Table 3 reports the characteristics of the vulcanizing formulation and those of the vulcanized product.

Example 5 (comparative)

A copolymer prepared in accordance to European Patent Application 407,937 and having the composition and properties as reported in Tables 1 and 2 has been used as a comparison.

Example 6 (comparative)

A copolymer prepared in accordance to European Patent Application 407,937 and having the composition and properties as reported in Tables 1 and 2 has been used as a comparison.

Example 7 (comparative)

A copolymer prepared in accordance to European Patent Application 407,937 and having the composition and properties as reported in Tables 1 and 3 has been used as a comparison.

Example 8

Operating conditions are as in Example 1 with the exception that the reactor is brought to pressure using a monomer mixture having the following molar composition:

VDF	4.5%
HFP	28.5%
MVE	37.0%
TFE	24.0%
ETHYLENE	6.0%

The operating temperature is 85°C and the pressure is 22 relative bar.
Feeding of the microemulsion and of PSA is performed as in Example 1.
The following additions are are also made:

- 46 g of BVE, subdivided into 20 additions, 2.3 g each, the first one executed before the start of polymerization and the subsequent ones at every 5% conversion.
- 3.2 g of CH_2I_2, subdivided into four additions, 0.8 g each, the first one executed at the beginning of polymerization and the subsequent ones at every 25% of monomer conversion.

During the polymerization, the pressure is maintained constant by feeding the monomers in the following molar ratios:

VDF	6.0%
HFP	7.0%
MVE	18.0%
TFE	34.0%
ETHYLENE	35.0%

After 184 minutes, 2,900 g of polymer are obtained
Tables 4 and 5 report data concerning the characteristics of the obtained polymer, the vulcanizing formulation and the vulcanized product.

Example 9

Operating conditions are as in Example 8 with the exception that the reactor is brought to pressure using a monomer mixture having the following molar composition:

VDF	5.5%
HFP	28.5%
MVE	38.0%
TFE	20.0%
ETHYLENE	8.0%

During the polymerization, the pressure is maintained constant by feeding a monomer mixture having the following molar composition:

VDF	10.0%
HFP	7.0%
MVE	18.0%
TFE	30.0%
ETHYLENE	35.0%

After 215 minutes, 2,780 g of polymer are obtained. Tables 4 and 5 report data concerning the characteristics of the obtained polymer, the vulcanizing formulation and the vulcanized product.

Example 10 (comparative)

Operating conditions are as in Example 8 with the exception that the reactor is brought to pressure using a monomer mixture having the following molar composition:

VDF	3.0%
MVE	68.5%
TFE	20.0%
ETHYLENE	8.5%

During the polymerization, the pressure is maintained constant by feeding a monomer mixture having the following molar composition:

VDF	4.0%
MVE	35.5%
TFE	20.5%
ETHYLENE	40.0%

After 156 minutes, 3,140 g of polymer are obtained. Tables 6 reports data concerning the characteristics of the obtained polymer, the vulcanizing formulation and the vulcanized product.

Chemical Resistance to Oils

The tests for resistance to oils mentioned in the examples have been performed using ASTM 3 oil containing 1% in volume of benzylamine dissolved therein, by maintaining a standard sample, vulcanized in press at 170°C for 10 minutes and post-treated in oven at 230 °C for 24 hours, immersed in oil for 3 days at 160 °C, using a sample/oil volume ratio of 1/10.
Tensile properties and sample volume variations have been measured after such treatment.
Results reported in the table refer to the percent variation in samples properties after treatment in oil.

Table 1

Example	1	2	3	4	5 (compar.)	6 (compar.)	7 (compar.)
Polymer Composition: - (% moles)							
VDF	27.7	28.0	43.0	63.0	53.8	58.2	77.8
HFP	7.6	7.5	14.0	14.0	21.5	-	21.6
PFMVE	17.0	16.8	7.5	7.5	-	17.7	-
E	21.0	21.3	17.5	8.0	-	-	-
TFE	26.4	26.4	18.0	7.1	23.9	23.4	-
BVE (bromovinylether)	0.3	-	-	0.4	0.8	0.7	0.6
- (% weight)							
VDF	19.5	20.0	32.8	47.9	37.1	40.5	59.4
HFP	12.6	12.6	25.0	24.9	34.8	-	38.6
MVE	31.4	31.2	14.8	14.7	-	32	-
E	6.5	6.7	5.8	2.7	-	-	-
TFE	29.1	29.5	21.5	8.4	25.8	25.4	-
BVE	0.9	-	-	1.3	2.4	2.1	2.0
Hydrogen	1.5	1.6	1.9	1.9	1.2	1.3	1.9
Mooney Viscosity $ML^{(2)}(1+10)$	28	37	52	18	26	46	44
T_g (DSC) (°C)	-10	-10	-12	-23	-9	-28	-23
Presence of Monomeric Diads							
VDF-E	Yes	Yes	Yes	Yes	No	No	No
HFP-E	Yes	Yes	Yes	Yes	No	No	No
TFE-E	Yes	Yes	Yes	Yes	No	No	No
HFP-VDF	Yes	Yes	Yes	Yes	Yes	No	Yes
TFE-VDF	Yes	Yes	Yes	Yes	Yes	Yes	No

Table 2

Example	1	2	3	5	6
Composition of Vulcanizing Formulation					
Polymer	100	100	100	100	100
Luperco 101 XL	3	-	-	3	3
Taic	3	-	-	3	3
ZnO	5	-	-	5	5
Bisphenol AF	-	2.5	1.9		
TB PCL	-	0.83		0.68	
$Ca(OH)_2$	-	6	6		
MgO	-	6	6		
Sulfolane	-	0.5	0.5		
Black MT	30	30	30	30	30
Formulation Characteristics					
ML N·m (pounds x inch)	1.13(10)	1.13(10)	1.92(17)	1.58(14)	1.58(14)
MH N·m (pounds x inch)	7.91(70)	8.36(74)	11.41(101)	10.96(97)	11.63(103)
t_{s2} (s)	69	294	234	60	54
t'_{90} (s)	192	918	366	288	261
Characteristics of Vulcanized Product after Post-Vulcanization:					
at 170°C for 10 min in press followed by oven aging at 230 °C for 24 hrs		(Stress-Strain) (ASTM D412-83)			
M 100 (MPa)	8.5	9.4	9.4	6.0	7.0
C.R. (MPa)	19	17	17.0	19	15
A.R. (%)	181	180	170	190	175
Shore A (ASTM D 2240-81)	71	81	79	73	72
Chemical Resistance Tests (Aging in ASTM 3 Oil Containing 1% Benzylamine)					
Variation M 100 (%)	+1.2	+5	+6.5	not measured for breakage	-4.4
Variation C.R. (%)	-3.4	-6	-14	-70.3	-23.2
Variation A.R. (%)	-2.4	-4	-7	-55.2	-10.9
Volume Variation (%)	+3.3	+3.5		+4	+3.8+

M = Modulus; C.R. = Load at Break; A.R. = Elongation at Break.

Table 3

Example		4		7
Vulcanizing Formulation	(% moles)			
Polymer		100		100
Luperco 101XL			3	
3				
Taic			3	
3				
ZnO			5	
5				
Black MT		30		30
Formulation Characteristics				
ODR 177 C ARC ±3 (ASTM D 2084-81)				
ML	N·m (pounds x inch)	0.57 (5)		1.81 (16)
MH	N·m (pounds x inch)	10.74 (95)		9.61 (85)
t_{s2}	(s)	66		60
t'_{90}	(s)	219		267
Characteristics of Vulcanized Product after Post-Vulcanization				
(at 170°C for 10 min followed by oven aging at 230°C for 24 hrs) (Stress-Strain) (ASTM D412-83)				
M 100	(MPa)		5.9	
5				
C.R.	(MPa)	18.6		18
A.R.	(%)	203		220
Shore A (ASTM D2240-81)		70		68
Low-Temperature Behavior	(ASTM D 1329)			
T.R. 10%	(°C)	-17.5		-17
T.R. 30%	(°C)	-14.4		-14
T.R. 50%	(°C)	-12.3		-12
Chemical Resistance				
Swelling in Methanol	(%)	+10		+80
T.R. = Temperature of Retraction				

Table 4

Example		8	9
Polymer Composition:			
	- (% moles)		
VDF		6.5	11.1
HFP		7.3	7.7
PFMVE		16.7	15.8
E		34.9	33.4
TFE		34.2	31.5
BVE		0.4	0.5
	- (% weight)		
VDF		4.7	8.1
HFP		12.5	13.3
PFMVE		31.5	30.1

Table 4 (continued)

Example		8	9
	- (% weight)		
E		11.1	10.7
TFE		38.9	36.2
BVE		1.3	1.6
Hydrogen		1.7	1.8
Mooney Viscosity ML(1+10)[121]		64	44
Tg (DSC)	(°C)	-3.5	-3.2
Presence of Monomeric Diads:			
VDF-E		Yes	Yes
HFP-E		Yes	Yes
TFE-E		Yes	Yes
HFP-VDF		Yes	Yes
TFE-VDF		Yes	Yes

Table 5

Example		8	9
Vulcanizing Formulation:			
Polymer		100	100
Luperco 101XL		3	3
Taic		3	3
ZnO		5	5
Black MT		30	30
Formulation Characteristics:			
ODR 177°C ARC ±3 (ASTM D 2084-81)			
ML	N·m (pounds x inch)	1.92 (17)	1.36 (12)
MH	N·m (pounds x inch)	8.81 (78)	8.25 (73)
t_{s2}	(s)	69	66
t'_{90}	(s)	219	204
Characteristics of Vulcanized Product after Post-Vulcanization			
(at 170°C for 10 min followed by oven aging at 230°C for 24 hrs)			
(Stress-Strain) (ASTM 412-83)			
M 100	(MPa)	10.2	9.9
C.R.	(MPa)	23.8	22.7
A.R.	(%)	201	190
Shore A (ASTM D 2240-81)		80	76
Chemical Resistance Tests			
(in ASTM 3 Oil + 1% Benzylamine - 3 Days - 160°C)			
Variation M 100	(%)	3.6	-2.5
Variation C.R.	(%)	-6.1	-4.5
Variation A.R.	(%)	0	4.9
Volume Variation	(%)	2.9	3

Table 6

Example / Polymer Composition:		10
	- (% moles)	
VDF		5.2
MVE		32.5
E		41.3
TFE		20.8
BVE		0.2
	- (% weight)	
VDF		3.7
MVE		59.8
E		12.8
TFE		23.0
BVE		0.6
Hydrogen		0.6
Mooney Viscosity $ML(1+10)^{121}$		53
Tg (DSC)	(°C)	-7.8
Vulcanizing Formulation		
Polymer		100
Luperco 101XL		3
Taic		4
ZnO		5
Black MT		30
Formulation Characteristics		
ODR 177°C ARC ±3 (ASTM D 2084-81)		
ML	N·m (pounds x inch)	1.70 (15)
MH	N·m (pounds x inch)	7.80 (69)
t_{s2}	(s)	66
t'_{90}	(s)	222
Characteristics of Vulcanized Product after Post-Vulcanization (230 °C - 24 hrs)		
(Stress-Strain) - (ASTM 412-83)		
M 100	(MPa)	10
C.R.	(MPa)	20.4
A.R.	(%)	193
Shore A (ASTM D 2240-81)		78

Claims

1. A fluoroelastomeric copolymer consisting essentially of: from 4 to 75% by mole of units deriving from vinylidene fluoride (VDF); from 12 to 40% by mole of units deriving from hexafluoropropene (HFP); from 2 to 35% by mole of units deriving from ethylene (E); from 2 to 60% by mole of units deriving from tetrafluoroethylene (TFE); and containing sequences consisting of the following monomeric diads: VDF-E, HFP-E, TFE-E.

2. The copolymer according to claim 1, wherein perfluoromethylvinylether (MVE) units partly substitute for the HFP units.

3. The copolymer according to claim 2, wherein MVE units wholly substitute for the HFP units, with the proviso that,

when the sum of MVE and E units is equal to or greater than 70%, then the copolymer has a molecular weight sufficiently high to give a Mooney viscosity of at least 10 $ML(1+10)^{121}$.

4. The copolymer according to anyone of the previous claims, containing from 0.05 to 2 moles per 100 moles of the other monomeric units, of monomeric units deriving from iodo and/or bromo olefins and/or bromoalkylvinylethers.

5. The copolymer according to anyone of the previous claims, containing iodine and/or bromine atoms at the ends of the polymeric chain.

6. An elastomeric copolymer, obtained by ionic vulcanization of a copolymer according to anyone of claims from 1 to 3.

7. An elastomeric copolymer, obtained by vulcanization with peroxides of a copolymer according to claim 4 or 5.

8. Use of a copolymer according to anyone of claims from 1 to 5 for manufacturing articles resistant to amine-containing motor oils.

9. A process for the preparation of fluoroelastomeric copolymers according to claims 1 to 5, consisting of copolymerizing the monomers in the presence of a free radical initiator, a surfactant and a dispersion, emulsion or microemulsion formed by perfluoropolyoxyalkylene and water.

Patentansprüche

1. Fluorelastomeres Copolymer, bestehend im wesentlichen aus: 4 bis 75 Mol-% Einheiten, abgeleitet von Vinylidenfluorid (VDF), 12 bis 40 Mol-% Einheiten, abgeleitet von Hexafluorpropen (HFP), 2 bis 35 Mol-% Einheiten, abgeleitet von Ethylen (E), 2 bis 60 Mol-% Einheiten, abgeleitet von Tetrafluorethylen (TFE) und enthaltend Sequenzen, bestehend aus den nachstehenden monomeren Diaden: VDF-E, HFP-E, TFE-E.

2. Copolymer nach Anspruch 1, worin Perfluormethylvinylethereinheiten (MVE) teilweise die HFP-Einheiten ersetzen.

3. Copolymer nach Anspruch 2, worin MVE-Einheiten vollständig die HFP-Einheiten ersetzen, mit der Maßgabe, daß, wenn die Summe von MVE- und E-Einheiten gleich oder größer als 70% ist, das Copolymer dann ein ausreichend hohes Molekulargewicht aufeist, damit eine Mooney-Viskosität von mindestens 10 $ML(1+10)^{121}$ erhalten wird.

4. Copolymer nach einem der vorangehenden Ansprüche, enthaltend pro 100 Mol der anderen Monomereinheiten 0,05 bis 2 Mol Monomereinheiten, die von Jod- und/oder Bromolefinen und/oder Bromalkylvinylethern abgeleitet sind.

5. Copolymer nach einem der vorangehenden Ansprüche, enthaltend Jod- und/oder Bromatome an den Enden der Polymerkette.

6. Elastomeres Copolymer, erhalten durch ionische Vulkanisation eines Copolymers nach einem der Ansprüche 1 bis 3.

7. Elastomeres Copolymer, erhalten durch Vulkanisation eines Copolymers nach Anspruch 4 oder 5 mit Peroxiden.

8. Verwendung eines Copolymers nach einem der Ansprüche 1 bis 5 zur Herstellung von Gegenständen, die gegen Aminenthaltende Motorenöle beständig sind.

9. Verfahren zur Herstellung von fluorelastomeren Copolymeren nach Ansprüchen 1 bis 5, bestehend aus Copolymerisieren der Monomere in Gegenwart eines freien radikalischen Starters, eines Tensids und einer Dispersion, Emulsion oder Mikroemulsion, gebildet aus Perfluorpolyoxyalkylen und Wasser.

Revendications

1. Copolymère élastomère fluoré consistant essentiellement en :

- de 4 à 75% en moles d'unités provenant du fluorure de vinylidène (VDF) ;
- de 12 à 40% en moles d'unités provenant de l'hexafluoropropène (HFP) ;
- de 2 à 35% en moles d'unités provenant de l'éthylène (E) ;
- de 2 à 60% en moles d'unités provenant du tétrafluoroéthylène (TFE) ;

et contenant des séquences consistant en les diades monomères suivantes : VDF-E, HFP-E, TFE-E.

2. Copolymère selon la revendication 1, dans lequel des unités de perfluorométhylvinyléther (MVE) remplacent partiellement les unités de HFP.

3. Copolymère selon la revendication 2, dans lequel des unités de MVE remplacent totalement les unités de HFP, à la condition que, lorsque la somme des unités de MVE et E est égale à ou supérieure à 70%, le copolymère a une masse moléculaire suffisamment élevée pour donner une viscosité Mooney d'au moins 10 ML $(1 + 10)^{121}$.

4. Copolymère selon l'une quelconque des revendications précédentes, contenant de 0,05 à 2 moles pour 100 moles des autres unités monomères, d'unités monomères provenant d'oléfines iodées et/ou bromées et/ou de bromoalkylvinyléthers.

5. Copolymère selon l'une quelconque des revendications précédentes, contenant des atomes d'iode et/ou de brome aux extrémités de la chaîne polymère.

6. Copolymère élastomère, obtenu par vulcanisation ionique d'un copolymère tel que défini à l'une quelconque des revendications 1 à 3.

7. Copolymère élastomère, obtenu par vulcanisation par des peroxydes d'un copolynére tel que défini à l'une des revendications 4 ou 5.

8. Utilisation d'un copolymère tel que défini à l'une quelconque des revendications 1 à 5 pour la fabrication d'articles résistants aux huiles a moteurs contenant des amines.

9. Procédé de préparation de copolymères élastomères fluorés tels que définis à l'une des revendications 1 à 5, consistant à copolymériser les monomères en présence d'un amorceur de radicaux libres, d'un agent tensio-actif et d'une dispersion, d'une émulsion ou d'une micro-émulsion formée par un perfluoropolyoxyalkylène et de l'eau.